



Performance of polyphosphazene based gel polymer electrolytes in combination with lithium metal anodes



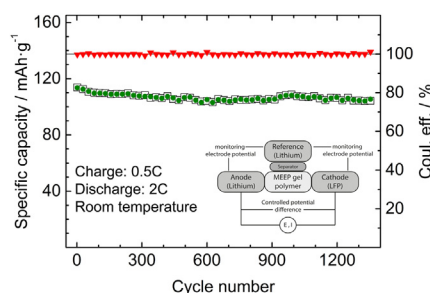
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HIGHLIGHTS

- Electrochemical stability window 0 V –4.4 V versus Li/Li⁺.
- Long term cycling stability in contact with lithium metal anode.
- 1350 cycles for a full cell with lithium anode without dendrite formation.
- MEEP based gel polymer: partial lithium ion conductivity of 0.1 mS cm⁻¹ (50 °C).

GRAPHICAL ABSTRACT



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ABSTRACT

This work presents a detailed study of the electrochemical performance of a polyphosphazene based gel polymer electrolyte in a lithium metal polymer cell. The polyphosphazene MEEP was chosen because of its favorable properties, such as good thermal and electrochemical stability versus lithium metal. In combination with a liquid electrolyte, consisting of 0.7 mol L⁻¹ LiBOB in EC/DMC, a high ionic conductivity of $9 \cdot 10^{-4}$ S cm⁻¹ at 30 °C was achieved. The electrochemical stability window ranges between 0 V and 4.4 V vs. Li/Li⁺ reference electrode. The gel polymer was drop coated onto the electrode materials and cross-linked to achieve high mechanical stability. The gel polymer showed a very good interface stability at lithium metal electrodes in the prepared full cells, where a stable SEI was formed during initial contact. The full cell tests delivered a stable cycling behavior with more than 1300 cycles and capacities higher than 110 mAh g⁻¹ at high discharge rates of 2C_D, without any indication for short circuits caused by lithium dendrites.

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1. Introduction

Due to the rising interest of applications for lithium secondary batteries which provide higher output voltage, higher specific capacity and longer cycle life, polymer electrolytes have been intensively studied in recent decades [1–3]. For secondary batteries like

lithium/sulfur or lithium/air batteries, lithium metal is still a desirable anode material due to its low weight, low cost and high specific capacity. The use of lithium metal is still challenging because of its safety issues caused by lithium dendrite growth during charging and thus its use in secondary batteries is still considered critically.

For lithium/polymer batteries several polymers like poly(ethylene oxide) (PEO) [4], polyacrylonitrile (PAN) [5,6], poly(methyl methacrylate) (PMMA) [7] or poly(vinylidene fluoride) (PVDF) [8,9] have been studied, but the ionic conductivity at lower temperatures is too low and thus inadequate for practical use at higher current

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densities. Therefore, the attention has turned to gel polymer electrolytes (GPEs). When cross-linked, the liquid component is incorporated into the polymer matrix and thereby preventing leakage of the liquid electrolyte and exhibiting high ionic conductivities from 10^{-4} to 10^{-3} S cm $^{-1}$ at room temperature.

In this work we focus on the electrochemical properties of a new polyphosphazene based gel polymer electrolyte, especially in combination with lithium metal anodes. As polymer matrix poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene (MEEP) was used. The combination with a liquid electrolyte made of 0.7 mol L $^{-1}$ lithium bis[oxalato]borate (LiBOB) in an ethylene carbonate/dimethylcarbonate (1:1 by weight) mixture lead to the gel polymer electrolyte. MEEP fulfills several requirements as a polymer matrix in gel polymer electrolytes [10], which are (a) easy production at low cost [11], (b) thermal stability [12], (c) good compatibility with the liquid electrolyte, resulting in good mechanical strength of the product [13] and (d) good electrochemical stability towards reduction and oxidation [14]. The functionality of the MEEP based gel polymer in direct contact to lithium metal and the examination of the gel polymer | lithium interface were investigated in full cells, using lithium iron phosphate (LFP) as cathode material and metallic lithium as anode.

2. Experimental

2.1. Materials

Ethylene carbonate (99.9%, Merck KGaA) and dimethyl carbonate (99.9% Merck KGaA) were directly used. Tetrahydrofuran (99.5%, VWR), *n*-pentane (98%, Baker) and toluene (99.7%, VWR) were freshly distilled from sodium benzophenone prior to use. Sulfuryl chloride (SO $_2$ Cl $_2$ 98%, Aldrich), phosphorous trichloride (PCl $_3$, 99%, Merck KGaA) and 2-(2-Methoxyethoxy)ethanol (C $_5$ H $_{12}$ O $_3$, 99% Merck KGaA) were freshly distilled before use. Sodium hydride (NaH, 60% w/w dispersion form in mineral oil, Aldrich), lithium bis(trimethylsilyl)amide (LiN(Si(CH $_3$) $_3$) $_2$, 97%, Aldrich), phosphorous pentachloride (PCl $_5$, sublimated under vacuum) and lithium bis(oxalato)borate (LiB(C $_2$ O $_4$) $_2$; 97%; Chemetall GmbH) were stored under Argon in a glove box. Chloroform-*d* (99.8 atom% D, Aldrich), lithium foil (Chemetall GmbH, 99.99%), platinum (Chempur, 99.99%, ϕ = 2 mm) and nickel (Alfa Aesar, 99.98%) were used as received Celite 545® (Merck KGaA) and the molecular sieve 4 Å (VRW) were dried at 140 °C for 48 h minimum before use. The dialysis tubes (Reichert Chemietechnik, molecular weight cut off 12,000–14,000 g mol $^{-1}$) for polymer purification were washed and cleaned with distilled water before use.

2.2. Polymer synthesis

The synthesis of the polyphosphazene MEEP proceeds according to a four step synthesis route by Wang et al. [15,16] with minor modifications [17] and a living cationic polymerization reaction, firstly reported by Allcock et al. [18]. Nucleophilic substitution of the chlorine atoms in [NPCl $_2$] $_n$ with sodium alcoholates leads to the desired MEEP. The detailed reaction route, thermal and electrochemical properties of a similar oligoether functionalized polyphosphazene was already published before [19].

119.5 mmol of lithium bis(trimethylsilyl)amide were dissolved in 300 mL of dry pentane. Freshly distilled phosphorous trichloride (114.6 mmol) was added drop wise within 30 min, while keeping the reaction temperature permanently below -5 °C. The reaction mixture was stirred for 30 min. Then sulfuryl chloride (106.1 mmol) was added drop wise under equal reaction conditions. After 30 min of stirring lithium chloride was precipitated, filtrated through Celite® and washed with 60 mL of dry *n*-pentane. After solvent

evaporation the phosphoranimine monomer Cl $_3$ PNSiMe $_3$ was vacuum distilled at 22 °C and 10^{-3} mbar. The monomer was received as a clear liquid with yields up to 70%. Afterward phosphorous pentachloride was dissolved in dry toluene with concentration of about 11 mmol L $^{-1}$ in toluene. The freshly prepared solution was added quickly to a monomer/toluene solution, thus an initiator-monomer ratio of 350:1 was reached. The polymerization product poly[dichloro-phosphazene] [NPCl $_2$] $_n$ was identified after 48 h by 31 P NMR. After solvent evaporation the transparent, viscous [NPCl $_2$] $_n$ was received. 31 P NMR (400 MHz, CDCl $_3$, 300 K): δ (ppm) ~ -17.97 .

3.6 g (150 mmol) of sodium hydride was suspended in 120 mL tetrahydrofuran and cooled to 0 °C. The freshly distilled (2-(2-methoxyethoxy)ethanol was added drop wise and the suspension was stirred for 1 h under hydrogen gas evolution. Then 8.7 g (74.9 mmol) of [NPCl $_2$] $_n$ dissolved in 50 mL tetrahydrofuran were added to the clear solution and stirred for 24 h while sodium chloride precipitated. Excess solvent was removed in a rotary evaporator. The product was purified in a dialysis tube (molecular weight cut off = 12,000–14,000 g mol $^{-1}$) against distilled water. After an evaporation of water and drying at 70 °C under vacuum for 2 days, the highly viscous, yellow honey like poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (MEEP) was received in a yield of 24.7 g (66.5 mmol, 88%). 1 H NMR (400 MHz, CDCl $_3$, 300 K): δ (ppm) = 3.33 (3H, s), 3.49 (8H, m), 4.03 (2H, s), 3.61 (2H, m). 13 C NMR (101 MHz, CDCl $_3$, 300 K): δ (ppm) = 59.06 (s), 65.13 (s), 70.86–70.29 (m), 72.09 (s). 31 P NMR (400 MHz, CDCl $_3$, 300 K): δ (ppm) = -8.34 (s).

2.3. Electrode preparation

Sodium carboxymethyl-cellulose (Na-CMC, WALOCCEL™ CRT 2000 PPA 12, Dow Wolff Cellulosics), lithium iron phosphate (LiFePO $_4$, P2, Süd-Chemie) and carbon black (Super P®, Timcal) were used as received. The preparation of electrodes was performed using the doctor blade method. At first the slurry was prepared by dissolving ~ 0.15 g Na-CMC in 3 mL water (Millipore, 2 h stirring). To the obtained binder solution 300 mg carbon black was added followed by 15 h stirring. Afterward 2.6 g LFP P2 (theoretical capacity $C_{\text{theo}} = 170$ mAh g $^{-1}$) and 3 mL water was added and stirred until the suspension was homogeneous. Finally the slurry was dispersed with a high energy stirrer (T 18 ULTRA-TURRAX®, IKA) for 1 h at 5000 rpm. Aluminum foil was etched in 5 wt.-% KOH (60 °C, 60 s, $d = 20$ μ m), cleaned with purified water and then directly coated with the slurry using a doctor blade (wet film = 120 μ m, dry film = 22–24 μ m). The sheets were dried in an oven at 80 °C for 15 h, stamped into discs of 12 mm diameter and dried for 48 h (120 °C at 10^{-3} mbar). The electrode composition was 85 wt.-% LFP P2, 10 wt.-% Super P and 5 wt.-% Na-CMC and had a load of ~ 2.85 mg cm $^{-2}$ $\hat{=}$ ~ 2.42 mg cm $^{-2}$ LFP.

2.4. MEEP gel polymer preparation and drop coating

In a dry room (H $_2$ O content < 10 ppm), a mixture of MEEP (including 5 wt.-% benzophenone as cross-linker) with the liquid electrolyte (LE) made of 0.7 mol L $^{-1}$ LiBOB in EC/DMC (1:1) was stirred for 2 h to ensure complete homogenization. The electrodes (LFP and metallic lithium) were drop coated with 40 μ L of the prepared electrolyte solution. While cooling the coated electrodes with dry ice, the polymer was simultaneously cross-linked by UV-irradiation within 7 min. The thickness of the gel polymer electrolyte coating was ~ 300 μ m. Using smaller amounts of the electrolyte solution in the drop coating process leads to thinner coatings. Anyway, a relatively thick electrolyte coating was used to enhance safety and long-term cycling capability by lowering the

probability of short circuits by direct contact of the working electrodes during the cell preparation. It is clear we had to accept higher internal resistances due to the thicker gel polymer coatings, but the good ionic conductivity of the MEEP gel polymers left this effect less crucial during constant current cycling. The coated electrodes were directly transferred into a glove box under argon atmosphere and assembled in Swagelok® cells.

2.5. Cell assembly and measurement

The CV curves were recorded with a computer controlled potentiostat Autolab PGStat302 N (Metrohm). The gel polymer electrolyte was a mixture of MEEP + 70 wt.-% liquid electrolyte (0.7 mol L^{-1} LiBOB in EC/DMC). The anodic oxidation limit was measured with a scan rate of 1 mV s^{-1} in the range from 2.5 V to 6 V using an inert polarizable platinum working electrode. The cathodic reduction limit was determined analogously in the range 2.5 V to -0.5 V by choosing an inert copper electrode as polarizable working electrode. All working electrodes had a diameter of 1 mm and were manually polished with abrasive paper down to grain P4000 before use.

Constant current cycling tests were carried out in Swagelok® cells using a 2-electrode measurement setup (Fig. 1). The third reference electrode was solely used to monitor the overvoltage-time dependence of the cathode and anode potentials separately. All cells were assembled under Argon atmosphere (glove box, $\text{O}_2 < 0.6 \text{ ppm}$, $\text{H}_2\text{O} < 0.2 \text{ ppm}$) and tested with a Series 4000 battery tester (Maccor). The constant current was related to LFP-content of the electrode taking a specific capacity of 170 mAh g^{-1} into account. The cells were cycled between 2.8 and 4 V vs. Li/Li⁺.

Lithium foil (99.99%, Rockwood Lithium) was stamped into discs ($d = 0.5 \text{ mm}$, $\phi = 12 \text{ mm}$) and used as counter- and reference electrode (CE, RE). The gel polymer electrolyte was a mixture of MEEP + 60 wt.-% liquid electrolyte (0.7 mol L^{-1} LiBOB in EC/DMC). For the full cell performance, the gel polymer coating functions as an electrolyte and as a separator at the same time (Fig. 1). The potential was monitored using the lithium counter electrode. The C-rate cycling had different discharge rates (discharge-rates: 0.1, 0.5, 1, 2, 3, 4, 5, 0.1, three cycles for each rate) and constant charge rates (charging 0.1C).

The ionic conductivity was determined with impedance spectroscopy. The gel polymer electrolyte membranes were sandwiched between two stainless steel electrodes with an area of 1 cm^2 . An AC impedance method with a frequency response analyzer Agilent E 4980 A (Agilent Technologies) was used, using a frequency range from 20 Hz to 2 MHz and amplitude of 40 mV. The impedance was recorded at different temperatures starting from -20°C to 90°C ,

controlled with a thermostat Julabo FP 45 (Julabo) under nitrogen atmosphere.

The lithium transference numbers were determined using a steady-state potentiostatic polarization method [20]. 2-Electrode Swagelok®-cells with two lithium electrodes according to Li|gel MEEP|Li were applied and controlled by a potentiostat Autolab PGStat302 N (Metrohm), together with Nova 1.6 (Ecochemie) software. The electrode surface areas were $A = 1.13 \text{ cm}^2$. The gel polymer electrolyte was a mixture of MEEP + 70 wt.-% liquid electrolyte (0.7 mol L^{-1} LiBOB in EC/DMC).

3. Results and discussion

3.1. Ionic transport and electrochemical stability

Fig. 2a shows the Arrhenius-plot of the prepared gel polymer electrolyte membranes. It is obvious that the ionic conductivity increases with increased amounts of liquid additive. At 30°C the highest ionic conductivity of $9 \cdot 10^{-4} \text{ S cm}^{-1}$ was obtained for MEEP + 70 wt.-% liquid electrolyte. However, the addition of 60 wt.-% liquid electrolyte has sufficient ionic conductivity for full cell application and still delivers enough mechanical stability when the gel polymer electrolyte is used as separator. The rapid decrease of the conductivity below 20°C can be explained by the crystallization of ethylene carbonate.

Fig. 2b shows the temperature dependent lithium transference numbers of the MEEP gel polymer. The values are in the range of

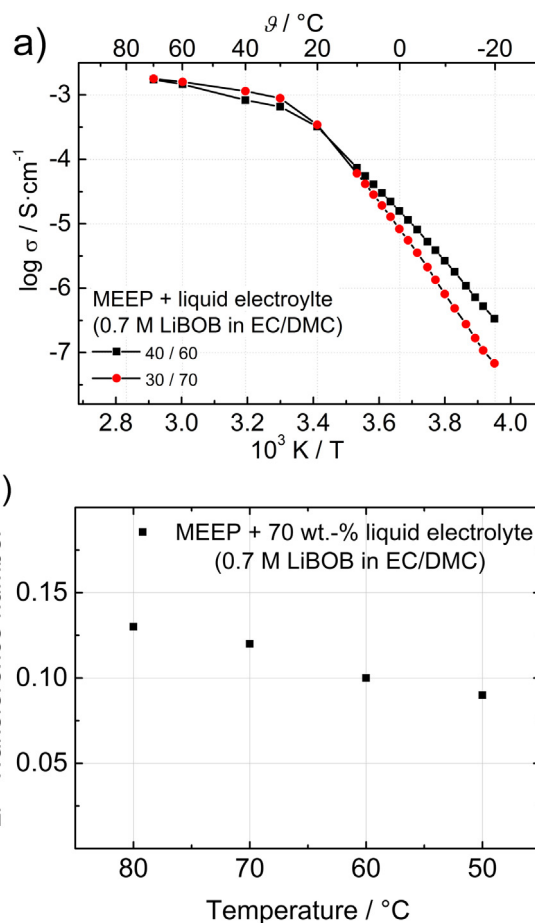


Fig. 2. a) Arrhenius-plot of the cross-linked MEEP gel polymer membranes with varying amounts of liquid electrolyte and b) lithium transference numbers of MEEP + 70 wt.-% liquid electrolyte.

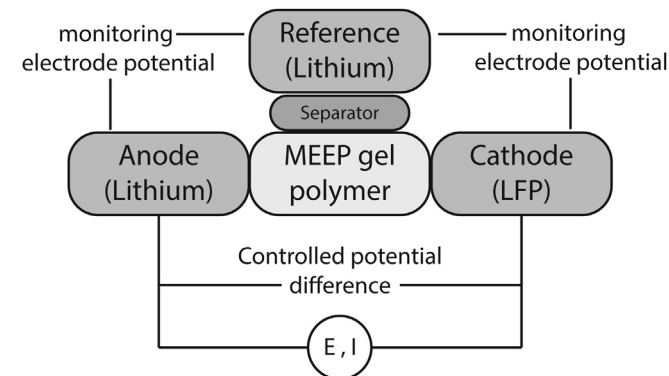


Fig. 1. Cell setup for the C-rate and constant current cycling tests with LiFePO₄ as cathode material.

$T_{Li+} = 0.09$ (50 °C) to $T_{Li+} = 0.13$ (80 °C). Thus, the partial lithium ion conductivity of 0.1 mS cm^{-1} at 50 °C can be obtained in a polarized steady state, with respect to $\sigma(\text{Li}^+) = T + (\text{Li}^+) \cdot \sigma(\text{total})$. Compared to solvent free polyphosphazene based solid polymer electrolytes, the partial lithium conductivity is increased by a factor of ~ 100 [19]. Anyway, the lithium transport is still lower as compared to pure liquid electrolytes due to strong lithium cation coordination in the polymer side chains. However, it is still high enough to operate full cells at room temperature.

The gel polymer electrolyte provides electrochemical stability against oxidation processes up to 4.4 V vs. Li/Li^+ (Fig. 3). The anodic oxidation at higher potentials leads to irreversible oxidation processes in the oligoether side chains of the polymer, most probably due to radical reactions induced by anodic hydrogen abstraction. The carbon radicals cause further radical reactions [21] and cross-linking due to radical recombination. Around 0 V the reversible lithium deposition and dissolution on the inert copper electrode is observed. As expected, the plating/stripping process is not completely reversible ($\sim 70\%$). Due to lithium plating in each constant voltage cycle, SEI formation losses decrease the plating/stripping efficiency in each cycle. Overall no significant decomposition reactions are observed in the required charge/discharge potential range from 0 V to 4.2 V, even at higher temperature (70 °C).

3.2. Thermal properties

The DSC heating curves (Fig. 4a) show three different processes in the cross-linked MEEP gel polymer electrolyte containing 70 wt.-% liquid. At -68°C the glass transition of the polymer MEEP can be obtained. Compared to the literature this value is higher than for pure MEEP ($\sim -80^\circ\text{C}$), because of the intermolecular cross-links, established by the curing of the polymer with benzophenone as a cross-linking agent and due to the addition of a lithium salt. At -17°C , an exothermic phase transition takes place and can be related to the recrystallization of ethylene carbonate inside the gel polymer matrix. This first order process can be observed in EC containing gel polymers due to the fast cooling (20 K min^{-1}) between the DSC measurements. At higher temperatures the observed heat flow results in an endothermic peak at 20°C and shows the melting of ethylene carbonate.

The TGA curve (Fig. 4b) shows a continuous loss of mass at temperatures above 130°C . The DTA shows three different processes taking place within the sample during the heating. At 133°C the evaporation of DMC can be observed. Compared to pure DMC the boiling temperature is shifted from 90°C (pure DMC) to

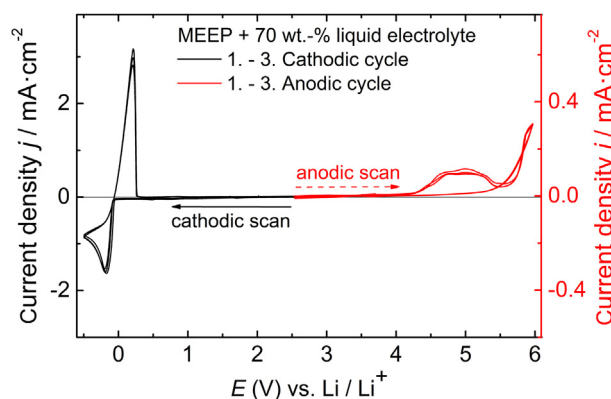


Fig. 3. Cyclic voltammogram at 70 °C of a cross-linked MEEP (+70 wt.-% liquid electrolyte) gel polymer membrane. Working electrodes: WE = Pt (anode) and WE = Ni (cathode). Scan rate: 1 mV s^{-1} .

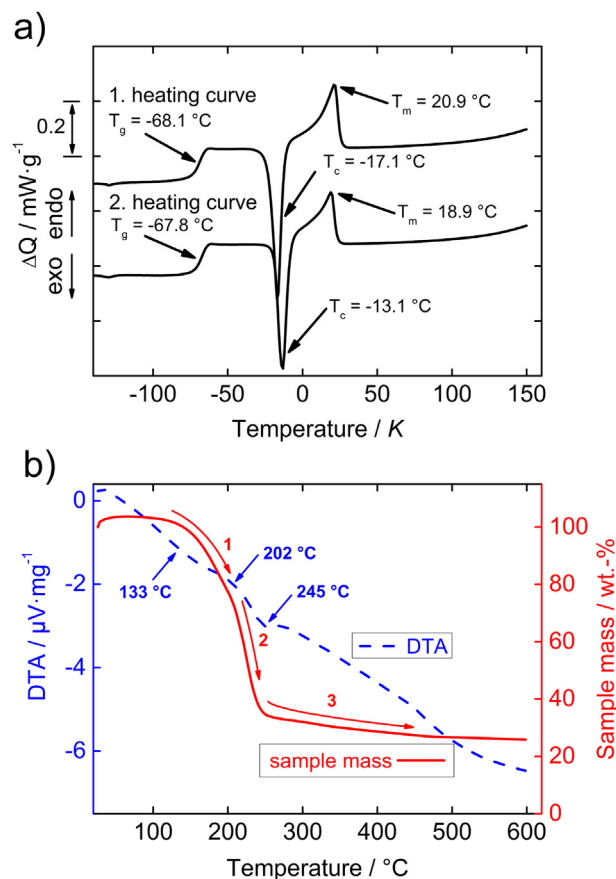


Fig. 4. a) First and second heating curve of the differential scanning calorimetry of the MEEP (+70 wt.-% liquid electrolyte) gel polymer membrane and b) TGA/DTA measurement.

higher values within the polymer matrix. Above 202°C a second degradation process takes place and is related to the depolymerization (random chain scission of poly ethylene oxide) of side chains, as compared to observations in PEO or PMMA polymers [22]. Above 245°C the decomposition of ethylene carbonate can be observed. At higher temperatures the loss of mass decreases very slow because the residuals mainly consist of P and N fragments derived from the polymer backbone [23]. These results confirm the observations of the DSC measurements and show the intrinsic thermal safety of the used gel polymer being stable up to $\sim 130^\circ\text{C}$.

3.3. Full cell tests with MEEP gel polymer coated LFP electrodes and lithium anodes

The full cells were measured in hermetically sealed cells with an oversized lithium electrode. A third lithium electrode was used as external reference while the cell potential was applied between the counter electrode and the working electrode. Although our full cells contained a third lithium metal reference electrode to monitor the electrode potentials separately and detect possible undesired resistances or overpotential changes, these data were not used for the full cell potentials as reported here. Nevertheless, they showed that no drastic changes of the single electrode overpotentials occurred during cycling.

The MEEP gel polymer was used as separator and electrolyte between the lithium anode and the LiFePO_4 cathode. The mean values of two constant current cycling experiments are displayed in Fig. 5a. They were cycled for five cycles at 0.1C (SEI formation) and

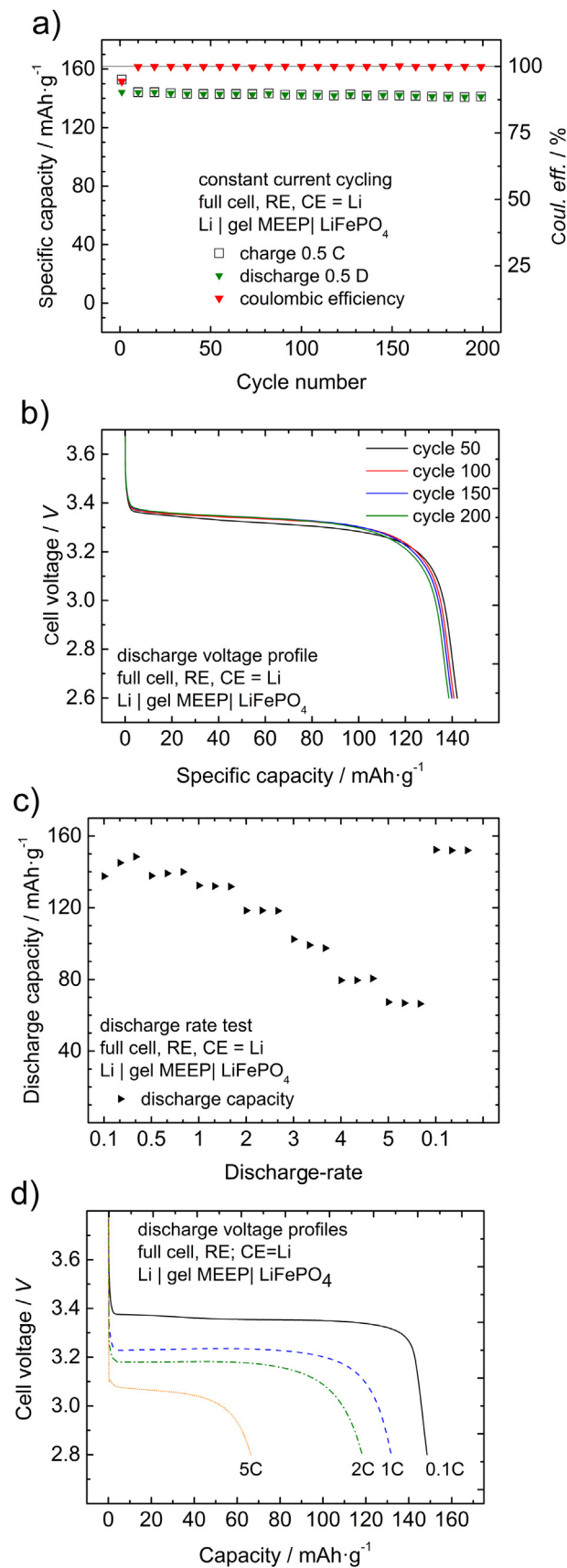


Fig. 5. a) Constant current cycling of a LFP/gel MEEP/Li full cell with a discharge rate of 0.5C, b) corresponding discharge voltage profile, c) discharge rates for the LFP/gel MEEP/Li full cell and d) the corresponding discharge voltage profile.

afterward continuously at 0.5C charge and 0.5C_D discharge rate. The cells delivered 144–141 mAh g⁻¹, which means that the loss in specific discharge capacity of the LFP cathode is only 3 mAh g⁻¹ within 200 cycles. After ~200–250 cycles dendrites shortened the cells. The total irreversible capacity loss referred to the lithium deposition/dissolution cycling at the lithium anode as summed up over 200 cycles resulted in $\sum C_{irr} = 40 \text{ mAh g}^{-1}$. The voltage profile of the full cell (Fig. 5b) shows a constant discharge plateau at ~3.4 V over 200 cycles. Although the cells were shortened by dendrites, the achieved capacities and the constant discharge plateau indicate a good compatibility of the gel polymer electrolyte in contact to LFP cathodes.

Fig. 5c shows the electrode performances under varying discharge rates (charging: 0.1C). The obtained discharge capacity is decreasing with increasing discharge rate. With an applied current of 0.1C the highest discharge capacity is ~152 mAh g⁻¹ (92% of C_{theo}) for the coated LiFePO₄ electrode in the full cell (last three cycles). The specific discharge capacity of the LFP cathode fades from 148 mAh g⁻¹ at 0.1C (=90% of C_{theo}) to 67 mAh g⁻¹ at 5C (40% of C_{theo}). The specific discharge capacity of the full cell is lower as compared to the use of liquid electrolytes due to higher internal resistance of the gelled polymer. The voltage profile (Fig. 5d) shows the characteristic discharge plateau for varying C-rates. Compared to liquid electrolytes the cell voltage decreases faster at higher C-rates, due to lower conductivity and lower lithium transference numbers.

Additionally, the two cells used for discharge-rate investigations were continuously cycled with 0.5C (charge) and 2C_D (discharge) rate afterward. Fig. 6a shows that these cells maintained a stable

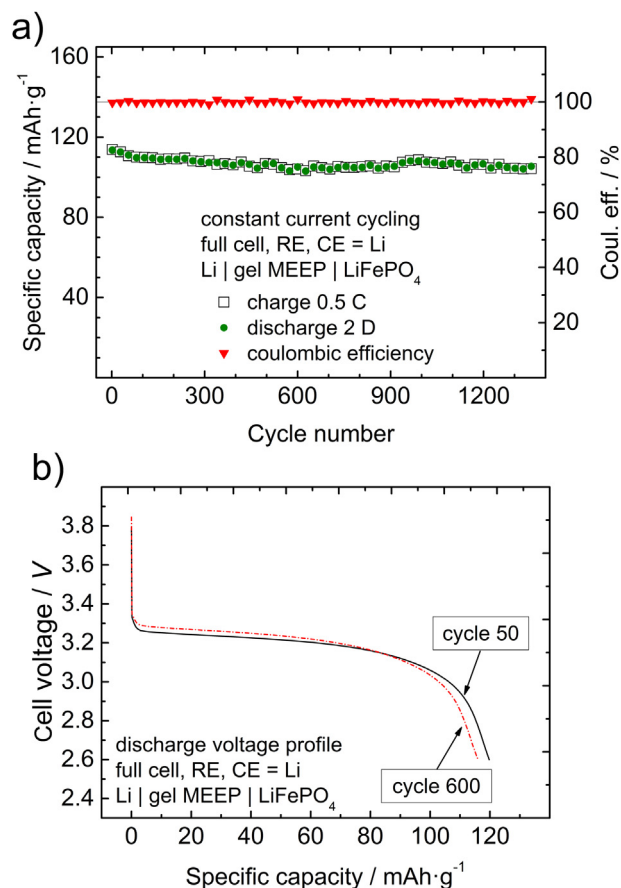


Fig. 6. a) Constant current cycling of a LFP/gel MEEP/Li full cell with higher discharge rate of 2C_D and b) corresponding discharge voltage profile.

cycling behavior for 1350 cycles with a specific discharge capacity of $\sim 115\text{--}105\text{ mAh g}^{-1}$ for the LFP cathode, which means 91% of the initial discharge capacity after 1000 cycles.

Since dendrite and SEI formation on lithium is dependent on the current density, a simple conclusion for this improvement is that a very stable SEI is formed during the low charging currents (lithium plating) during the discharge-rate investigations (24 cycles at 0.1C compared to 5 cycles at 0.1C in the former test (Fig. 5a). Due to the lower sum of irreversible capacity losses caused by the lithium anode of $\sum C_{\text{irr}} = 28\text{ mAh g}^{-1}$ over 200 cycles, the cells could cycle over 4500 times using a fivefold lithium excess in the anode (based on calculation). The coulombic efficiencies for a single charge/discharge cycle were always at least 99.3% or higher.

More evidence for the good SEI stability which leads to high constant current cycle numbers can be found in the SEM images of two cycled lithium anodes. Fig. 7a shows the surface of the lithium metal anode cycled with MEEP/LiBOB/EC/DMC gel polymer. After 250 cycles the surface remains very smooth without cracks or dendrites.

Fig. 7b shows the SEM image of the lithium surface of a cycled lithium metal anode using a MEEP/PC/LiDFOB gel polymer. Although the discharge rates are the same (0.5C charge/0.5C_D discharge) the surface of the anode remained very porous and cracked. On this rough surface the lithium plating is very

inhomogeneous and leads to a higher surface area which can promote lithium dendrite growth during charging. The SEM images support the experiences about the good lithium interface stability of the MEEP/LiBOB gel polymer which was already observed in the previous cycling test.

4. Conclusion

In this work we presented the first full cell with an inorganic polyphosphazene based gel electrolyte in combination with a lithium metal anode exhibiting more than 1300 cycles. The use of the polyphosphazene MEEP considerably enhanced the lifetime. This was attributed to its ability to form and continuously repair a safe SEI layer. High ionic conductivity, an electrochemical stability window of 4.4 V versus lithium metal, a good capacity retention and a long cycle life were obtained. Different charging/discharging test conditions demonstrated a very good SEI stability for the MEEP/LiBOB/EC/DMC gel polymer. Together with the suppression of any extensive dendrite formation up to higher charge/discharge rates, the results make the MEEP based gel polymer electrolytes an interesting candidate for cells with lithium metal anodes with combined separator/electrolyte function. It will be interesting to analyze further chemical variation of the parent polyphosphazene as well as extensive tests with thinner electrolyte membranes.

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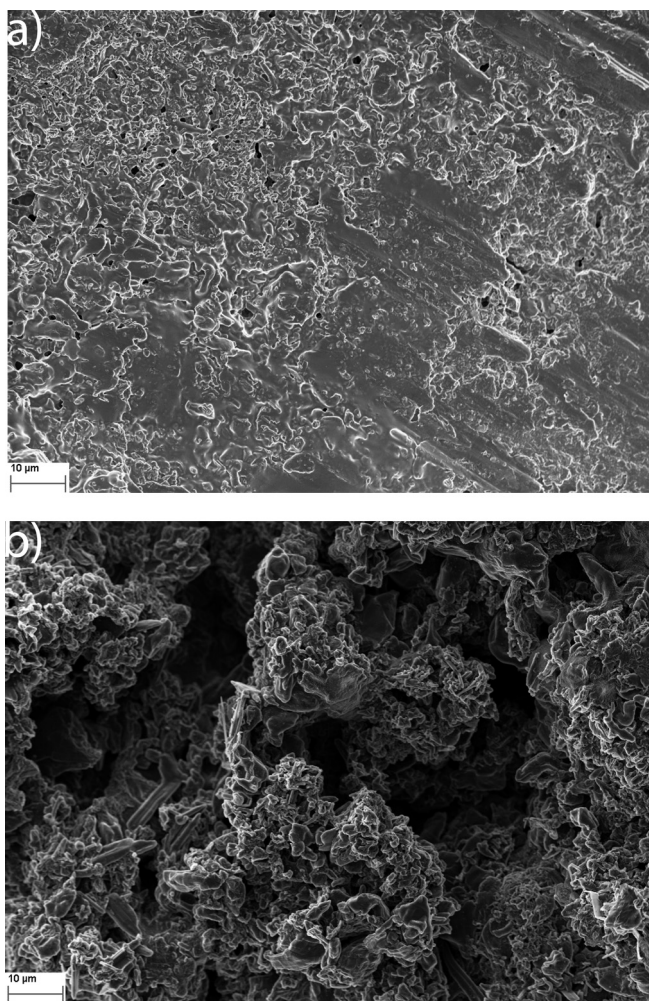


Fig. 7. a) SEM image of the lithium metal anode surface cycled with MEEP/LiBOB gel polymer and b) SEM image of a lithium metal anode surface cycled with MEEP/PC/LiDFOB gel polymer.